

Low-frequency Raman scattering in model disordered solids: percolators above threshold.

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Abstract

The Raman coupling coefficients of site- and bond-percolators at concentration higher than percolation threshold are computed for two scattering mechanisms: Bond Polarizability (BPOL) and Dipole-Induced-Dipole (DID). The results show that DID does not follow a scaling law at low frequency, while in the case of BPOL the situation is less clear. The numerically computed frequency dependence in the case of BPOL, which can be considered a good scattering mechanism for a wide class of real glasses, is in semiquantitative agreement with experimental results.

I. INTRODUCTION

Raman scattering is a very powerful technique to study the vibrational dynamics of solids, and more so in disordered solids where the vibrational eigenvectors are not propagating plane waves and the law of pseudo-momentum conservation does not hold. This has the consequence that all modes, to some extent, can in principle scatter the light. From the experimental point of view, the Raman spectra of most glasses show two characteristic features at low frequency: the so-called quasi elastic scattering excess (QESE) in the energy range below $\approx 5 \div 10 \text{ cm}^{-1}$, and the boson peak, a relatively broad band peaked in the range $10 \div 100 \text{ cm}^{-1}$ depending on the nature of the glass [1,2].

The QESE manifests itself in the fact that by rising the temperature, the scattering intensity in the indicated range grows more rapidly than predicted by the Bose-Einstein statistics (which is not the case for the boson peak). This indicates that the QESE originates either from two-”phonon” processes or from anharmonic degrees of freedom consisting possibly of some sort of generalized two-level systems [3] that are dealt with by the so-called soft potential model [4]. At low enough temperature the QESE contribution to the scattering becomes negligible, and what is left in the spectrum at frequency higher than a few wavenumbers derives presumably from harmonic, acoustic-like vibrations of low frequency. In the following we will focus our attention on these vibrational modes.

Starting from the work of Shuker and Gammon [5] many authors [6–8] with different approaches and approximations showed that the Stokes intensity scattered at first order by harmonic vibrations in disordered solids can be written as

$$I(\omega, T) \propto \frac{1}{\omega} [n(\omega, T) + 1] C(\omega) g(\omega) \quad (1)$$

where $n(\omega, T)$ is the Bose-Einstein population factor, $C(\omega)$ is the average light-vibration coupling coefficient of the modes having frequency between ω and $\omega + d\omega$ [9], and $g(\omega)$ is the density of vibrational states.

The frequency-dependence of $I(\omega, T)$, or equivalently of $C(\omega)$, has been the object of much debate, and in particular the question concerns whether they are scaling quantities

or not [11–19], both in real glasses and in model disordered systems. The investigation of the frequency dependence of $C(\omega)$ for model disordered solids is becoming more and more attractive also in view of the recent demonstration, by Fontana and coworkers [20,21], that a combination of Raman and specific heat experiments allows for the determination of the density of vibrational states with an accuracy comparable to neutron scattering experiments, and therefore provides the functional form of $C(\omega)$.

In a previous paper [18] we have studied this problem in detail for the case of percolating networks at percolation threshold concentration, showing that the scaling laws, if any, are so strongly model dependent, that it is practically impossible to extract reliable information on the dynamics of the system from the knowledge of $C(\omega)$.

In the present work we will study percolators having a concentration higher than threshold: although it is not granted that these systems can reproduce the scattering properties of real disordered systems (even neglecting QESE), they are certainly more realistic than percolators at threshold, but share with the latter a basic simplicity. In this paper we devote most of our attention to bond percolators rather than to site percolators: indeed, in our opinion, these systems could represent a reference model for covalent, network forming glasses.

We report the calculation of the Raman coupling coefficients of percolators at high mass concentration (up to 98%), and show that also in these more "realistic" model solids the existence of scaling behavior of the Raman coupling coefficient is highly questionable.

In order to calculate the Raman coupling coefficient $C(\omega)$ it is not enough to know the vibrational dynamics, but it is also necessary to specify the mechanism by which the vibrations modulate the electric polarizability of the scattering units. In the bond-polarizability mechanism (BPOL), the electric polarizability is localized on the bonds that link the atoms and is directly modulated by the change in bond lengths produced by the vibrations. In the dipole-induced-dipole (DID) mechanism the polarizable units are the atoms and the vibrations, by changing the interatomic distances, modulate the dipolar interaction between them and thus their polarizability. Very roughly speaking, BPOL may be expected to dominate

in covalent materials, while DID has been shown to be the most important mechanism for rare gases and, in general, in the presence of van der Waals interactions. However, in real glasses the situation will not be that simple; for example, in a molecular solid like a polymer we might expect BPOL to dominate for frequencies corresponding to intramolecular modes and DID for frequencies corresponding to intermolecular ones. Moreover, even for network forming glasses the two scattering mechanisms might coexist in the same frequency range. These considerations imply that one should be very cautious in establishing a strict correspondence between the results of simulation and experiments. Nevertheless, due to the difficulties of simulating real glassy samples large enough to give access to the low frequency region where the scaling laws are assumed to hold, we think that the simulation of model systems remains an important tool for the study of the dynamics of topologically disordered solids.

II. RESULTS AND DISCUSSION

The numerical method we use is the method of moments [22,18]; the calculation and the expedients that ensure good coverage with large systems were discussed at length in ref. [18], together with the different forms the equations of the moments take for BPOL and DID, and we refer the reader to this reference for the details.

The systems we study are 3-dimensional site- and (mostly) bond-percolators consisting of identical masses linked by identical springs; each mass is assigned a single vibrational degree of freedom and periodic boundary conditions are imposed. Mass and/or spring disorder could easily be introduced in the calculation, but its effect is mainly to distinguish between acoustic-like modes at low frequency, and optical-like ones in the high frequency range, while here we are interested in the low frequency acoustic spectrum. We studied different concentrations ranging from percolation threshold to 80% (for site percolators) and 70% (for bond percolators). The linear dimension of the samples was $L = 85$ [23]. Following the procedures described in ref. [18] we have computed the density of vibrational states and

the Raman coupling coefficients for the two scattering mechanisms, $C_{DID}(\omega)$ and $C_{BP}(\omega)$. The density of states exhibits the usual crossover from phonon-like to fracton-like behavior already observed in several papers.

In Fig. 1 we report the log-log plot of DID and BPOL $C(\omega)$'s for site percolators at a mass concentration $c_M = 0.8$, together with the density of states. Hereafter, the frequency ω is in units of the maximum frequency. In the preliminary results ($c_M = 0.5$) of ref. [18] we observed that the phonon-fracton crossover frequency of the density of states is higher than that of the coupling coefficients. A similar behavior is observed in Fig. 1; indeed: (i) the density of states follows a phonon-like behavior up to a frequency ($\omega \approx 0.5$) higher than the crossover frequency observed in DID and BPOL coupling constants (i.e. $\omega \approx 0.2$), and (ii) none of the slopes of $C_{DID}(\omega)$ and $C_{BP}(\omega)$ observed in the "fracton" frequency region has direct connection with the slopes at threshold [18].

In Fig. 2 are shown the BPOL coupling coefficients $C_{BP}(\omega)$ for bond percolators at bond concentrations ranging from $c_B = 0.249$ (percolation threshold) to $c_B = 0.7$. It is worth to note that these two extreme *bond* concentrations correspond to *mass* concentrations c_M of 0.35 and 1 respectively (to a bond concentration of 0.5 corresponds a mass concentration of 0.98), so that bond percolators with c_B in the range between 0.5 and 1 could represent a model for real network forming glasses.

An interesting new feature can be observed in Fig. 2: as c_B is increased the low frequency part of the spectrum acquires a concentration-dependent slope, $S_L(c)$, that is appreciably *lower* than the slope at percolation threshold ($S(c = c_T) \approx 1.6$). This is contrary to what would be expected by analogy to the phonon-fracton crossover observed in the density of states, which produces a *higher* slope at low frequency. The crossover frequency observed in the present case increases with concentration. It is likely that a larger "phononic" slope is present as well, but at too low a frequency to be observed in our samples. In any case a phonon-like contribution with slope $S > 2$ starts to be observed at $c_B = 0.35$, and at $c_B = 0.5$ it covers the whole low frequency part of the spectrum ($\omega < 0.1$); at this and higher concentration, the high-frequency slope is intermediate between those found at low

frequency and at threshold.

In Fig. 3 we report the $C_{DID}(\omega)$ coupling coefficients for bond percolators with concentrations ranging from $c_B = 0.249$ to $c_B = 0.7$. As the concentration increases, the low frequency "scaling" [24] part of the spectrum at threshold concentration is more and more covered from both sides: from low frequency by the "phononic" slope and from high frequency by a roundish spectrum to which no slope can reasonably be associated. Already at a bond concentration $c_B = 0.325$, corresponding to a mass concentration $c_M \approx 0.79$, the threshold slope ($S(c_T) \approx 0.2$) has completely disappeared.

The main motivation of the present investigation was to check in some detail, and on simple models, whether the claimed scaling behavior of the low frequency coupling coefficient $C(\omega)$ would survive in a situation less unrealistic than percolation threshold.

The answer is definitely negative for DID, and it may be worth to clarify shortly why the authors of ref. [19] may have concluded that at a concentration $c_B = 0.31$ (comparable to our Fig. 3(b)) the spectrum does scale above the crossover.

From Fig. 3(b) it is clear that the slope above the crossover ($S(c > c_T) \approx 0$) has nothing to do with that at low frequency in the threshold spectrum of Fig. 3(a) ($S(c_T) \approx 0.2$). The fact is that in ref. [19] it is the reduced Raman intensity,

$$J(\omega) = I(\omega)/n(\omega) + 1 \propto C(\omega)\rho(\omega) \propto C(\omega)\omega^{-0.67}$$

that is plotted, and not $C(\omega)$. Being $C(\omega)$ in the frequency range of interest only slightly roundish (see Fig. 3(b)), $J(\omega)$ will have a slightly rounded look superimposed on a line of slope ≈ -0.5 , that is exactly what is observed in ref. [19], Fig. 2(b). The same qualitative arguments apply to their Fig. 2(a). The scaling of $C_{DID}(\omega)$ found in ref. [19] is therefore an artifact that arises from plotting $J(\omega)$, rather than $C(\omega)$, on a shrunk vertical scale.

The situation is more complex for BPOL which, as mentioned, is expected to be the dominant mechanism for covalent solids. More than one power law is observed in this case. The origin of the new low-frequency slope that emerges as the concentration is increased, is not clear to us. In any case, that slope is not very different from the one at percolation

threshold, and compares rather favourably with the values suggested from combined Raman-neutron scattering [25] and Raman-thermal [20,21] experiments, that yield $C(\omega) \propto \omega^{0.7 \pm 1}$.

Though in our opinion one should be very cautious and await calculations on more realistic systems, it is not unconceivable that these values reflect the slopes computed here. The fact that slopes of the order of unity are observed in many different glasses suggests that they are the result of very general properties of BPOL-like scattering mechanisms in disordered media: therefore, after all, it is not too much of a surprise if a simple model like the present one has the same qualitative features. On the other hand the appearance of a *smaller* slope at very low frequency could be an indication that, also in network forming glasses, the coupling coefficient $C(\omega)$ reaches a constant value when ω approaches zero. Indeed this kind of non-scaling behavior has been recently found in a (simulated) model of fragile glass [26].

In conclusion, in the present work we have shown that a large variety of behavior is found for $C(\omega)$ at low frequency. It is difficult to reach a definite conclusion as to the validity of scaling laws for BPOL, but we feel confident in asserting that extracting quantitative information on the system's parameters from the measured spectra on the basis of scaling arguments, is potentially misleading and at present unreliable.

On the other hand, the numerically computed frequency dependence of $C_{BP}(\omega)$ is in semiquantitative agreement with experimental findings. Such capability of simple percolating structures to reproduce widespread properties of disordered solids was previously pointed out by Sheng and Zhou [27], who by using site percolators above threshold were able to reproduce the plateau of low-temperature thermal conductivity. It might be interesting to check whether the other common feature of Raman scattering in glasses, i.e. the boson peak, is a characteristic of high-concentration percolators as well.

FIGURE CAPTIONS

FIG. 1 - Site percolator, $L = 85$, $c = 0.8$, 1 realization. (a) density of states; (b) $C_{DID}(\omega)$; (c) $C_{BP}(\omega)$. For graphical convenience the traces are vertically shifted.

FIG. 2 - $C_{BP}(\omega)$ for bond percolators, $L = 85$, average of 10 realizations, at various bond concentrations. (a) $c_B = 0.249$; (b) $c_B = 0.325$; (c) $c_B = 0.35$; (d) $c_B = 0.4$; (e) $c_B = 0.5$; (f) $c_B = 0.7$. For graphical convenience the traces are vertically shifted.

FIG. 3 - $C_{DID}(\omega)$ for bond percolators, $L = 85$, average of 10 realizations, at various bond concentrations. (a) $c_B = 0.249$; (b) $c_B = 0.325$; (c) $c_B = 0.4$; (d) $c_B = 0.7$. For graphical convenience the traces are vertically shifted.

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